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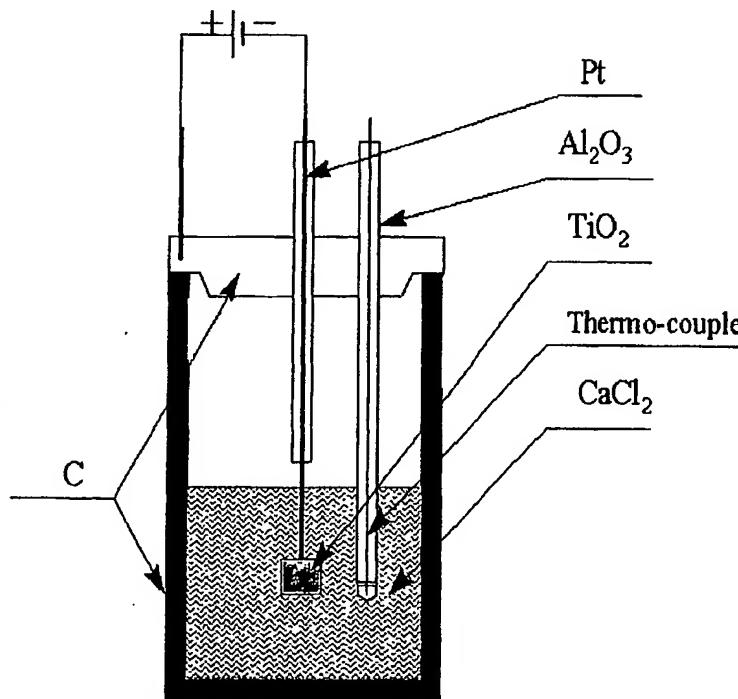
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(71) Applicant (for all designated States except US): BHP BILLITON INNOVATION PTY LTD [AU/AU]; 600 Bourke Street, Melbourne, Victoria 3000 (AU).  
(72) Inventors; and  
(75) Inventors/Applicants (for US only): STREZOV, Les [AU/AU]; 7 Marin Street, Adamstown, New South Wales
- 2289 (AU). RATCHEV, Ivan [AU/AU]; 2 Young Street, Georgetown, New South Wales 2298 (AU). OSBORN, Steve [AU/AU]; 15 Robertson Road, Valentine, New South Wales 2280 (AU).  
(74) Agent: GRIFFITH HACK; 509 St Kilda Road, Melbourne, Victoria 3004 (AU).  
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[Continued on next page]

(54) Title: REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL



(57) Abstract: A method of reducing a metal oxide, such as titania in a solid state in an electrolytic cell is disclosed. The electrolytic cell includes an anode, a cathode, and a molten electrolyte. The electrolyte includes cations of a metal that is capable of chemically reducing the metal oxide. The metal oxide in a solid state is immersed in the electrolyte. The method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

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Schematic of the experimental set up

Best Available Copy



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

**Published:**

— *with international search report*

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## REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL

The present invention relates to reduction of metal oxides in a solid state in an electrolytic cell.

5

The present invention was made during the course of an on-going research project on solid state reduction of titania ( $TiO_2$ ) carried out by the applicant.

10

During the course of the research project the applicant carried out experimental work on the reduction of titania using an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten  $CaCl_2$ -based electrolyte in the crucible, and a range of cathodes that included solid titania.

15

One objective of the experimental work was to reproduce the results reported in International application PCT/GB99/01781 (publication no. WO99/64638) in the name of Cambridge University Technical Services Limited and in technical papers published by the inventors of that International application.

20

The Cambridge International application discloses two potential applications of a "discovery" in the field of metallurgical electrochemistry.

25

One application is the direct production of a metal from a metal oxide.

30

In the context of this application, the "discovery" is the realisation that an electrolytic cell can be used to ionise oxygen contained in a metal oxide so that the oxygen dissolves in an electrolyte. The Cambridge International application discloses that when a suitable potential is applied to an electrolytic cell with a metal oxide as a cathode, a reaction occurs whereby

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oxygen is ionised and is subsequently able to dissolve in the electrolyte of the cell.

5 European patent application 9995507.1 derived from the Cambridge International application has been allowed by the European Patent Office.

10 The allowed claims of the European patent application *inter alia* define a method of electrolytically reducing a metal oxide (such as titania) that includes operating an electrolytic cell at a potential at an electrode formed from the metal oxide that is lower than the deposition potential of cations in the electrolyte at a surface of the electrode.

15 20 The Cambridge European patent application does not define what is meant by deposition potential and does not include any specific examples that provide values of the deposition potential for particular cations.

25 However, submissions dated 2 October 2001 to the European Patent Office by the Cambridge patent attorneys, which pre-dated the lodgement of the claims that were ultimately allowed, indicate that they believe that the decomposition potential of an electrolyte is the deposition potential of a cation in the electrolyte.

30 Specifically, page 5 of the submissions state that:

"The second advantage described above is achieved in part through carrying out the claimed invention below the decomposition potential of the electrolyte. If higher potentials are used then, as noted in D1 and D2, the cation in the electrolyte deposits on the metal or semi-metal compound. In the example of D1, this leads to calcium deposition and therefore consumption of this

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reactive metal.....During operation of the method, the electrolytic cation is not deposited on the cathode".

Contrary to the findings of Cambridge, the  
5 experimental work carried out by the applicant has  
established that it is essential that the electrolytic  
cell be operated at a potential that is above the  
potential at which  $\text{Ca}^{++}$  cations in the electrolyte can  
deposit as Ca metal on the cathode.

10

Accordingly, the present invention provides a  
method of reducing a metal oxide in a solid state in an  
electrolytic cell, which electrolytic cell includes an  
anode, a cathode, a molten electrolyte, the electrolyte  
15 includes cations of a metal that is capable of chemically  
reducing the metal oxide, and the metal oxide in a solid  
state immersed in the electrolyte, and which method  
includes a step of operating the cell at a potential that  
is above a potential at which cations of the metal that is  
20 capable of chemically reducing the metal oxide can deposit  
as the metal on the cathode, whereby the metal chemically  
reduces the metal oxide.

The applicant does not have a clear understanding  
25 of the electrolytic cell mechanism at this stage.

Nevertheless, whilst not wishing to be bound by  
the comments in this and the following paragraphs, the  
applicant offers the following comments by way of an  
30 outline of a possible cell mechanism.

The experimental work carried out by the  
applicant produced evidence of Ca metal dissolved in the  
electrolyte. The applicant believes that, at least during  
35 the early stages of operation of the cell, the Ca metal  
was the result of electrodeposition of  $\text{Ca}^{++}$  cations as Ca  
metal on electrically conductive sections of the cathode.

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The experimental work was carried out using a CaCl<sub>2</sub>-based electrolyte at a cell potential below the decomposition potential of CaCl<sub>2</sub>. The applicant believes  
5 that the initial deposition of Ca metal on the cathode was due to the presence of Ca<sup>++</sup> cations and O<sup>--</sup> anions derived from CaO in the electrolyte. The decomposition potential of CaO is less than the decomposition potential of CaCl<sub>2</sub>. In this cell mechanism the cell operation is dependent, at  
10 least during the early stages of cell operation, on decomposition of CaO, with Ca<sup>++</sup> cations migrating to the cathode and depositing as Ca metal and O<sup>--</sup> anions migrating to the anode and forming CO and/or CO<sub>2</sub> (in a situation in which the anode is a graphite anode).

15

The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in the early stages of cell operation and thereafter  
20 dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania.

The applicant also believes that at later stages  
25 of the cell operation part of the Ca metal that deposited on the cathode was deposited directly on partially deoxidised titanium and thereafter participated in chemical reduction of titanium.

30

The applicant also believes that the O<sup>--</sup> anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced CO and/or CO<sub>2</sub> (and in some instances CaO) and released electrons that facilitated electrolytic deposition of Ca metal on the  
35 cathode.

Preferably the cathode is formed at least in part

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from the metal oxide.

Preferably the method includes operating the cell at the potential that is above the potential at which  
5 cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode so that the metal deposits on the cathode.

Preferably the metal deposited on the cathode is  
10 soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the metal oxide.

In a situation in which the metal oxide is a  
15 titanium oxide, such as titania, it is preferred that the electrolyte be a  $\text{CaCl}_2$ -based electrolyte that includes  $\text{CaO}$  as one of the constituents of the electrolyte. In this context, it is noted that the present invention does not require the addition of substantial amounts of  $\text{CaO}$  to the  
20 electrolyte.

In such a situation it is preferred that the cell potential be above a potential at which  $\text{Ca}$  metal can deposit on the cathode, i.e. at a potential that is above  
25 the decomposition potential of  $\text{CaO}$ .

The decomposition potential of  $\text{CaO}$  can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and  
30 electrolyte composition.

In a cell containing  $\text{CaO}$  saturated  $\text{CaCl}_2$  at 1373K (1100°C) and a graphite anode this would require a minimum cell potential of 1.34V.

35

It is also preferred that the cell potential be below the potential at which  $\text{Cl}^-$  anions can deposit on the

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anode and form chlorine gas, i.e. the decomposition potential of CaCl<sub>2</sub>.

5 In a cell containing CaO saturated CaCl<sub>2</sub> at 1373K (1100°C) and a graphite anode this would require that the cell potential be less than 3.5V.

10 The decomposition potential of CaCl<sub>2</sub> can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and electrolyte composition.

15 For example, a salt containing 80% CaCl<sub>2</sub> and 20% KCl at a temperature of 900K (657°C), decomposes to Ca (metal) and Cl<sub>2</sub> (gas) above 3.4V and a salt containing 100% CaCl<sub>2</sub> at 1373K (1100°C) decomposes at 3.0V.

20 In general terms, in a cell containing CaO-CaCl<sub>2</sub> salt (not saturated) at a temperature in the range of 600-1100°C and a graphite anode it is preferred that the cell potential be between 1.3 and 3.5V.

25 The CaCl<sub>2</sub>-based electrolyte may be a commercially available source of CaCl<sub>2</sub>, such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO.

30 Alternatively, or in addition, the CaCl<sub>2</sub>-based electrolyte may include CaCl<sub>2</sub> and CaO that are added separately or pre-mixed to form the electrolyte.

It is preferred that the anode be graphite or an inert anode.

35 The applicant found in the experimental work that there were relatively significant amounts of carbon transferred from the graphite anode to the electrolyte and

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to a lesser extent, to the titanium produced at the cathode under a wide range of cell operating conditions.

5 Carbon in the titanium is an undesirable contaminant. In addition, carbon transfer was partially responsible for low energy efficiency of the cell. Both problems could present significant barriers to commercialisation of electrolytic reduction technology.

10 The applicant also found that the dominant mechanism of carbon transfer is electrochemical rather than erosion and that one way of minimising carbon transfer and therefore contamination of titanium produced at the cathode by electrochemical reduction of titania is 15 to position a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms between the cathode and the anode and thereby prevent migration of carbon to the cathode.

20 Accordingly, in order to minimise contamination of titanium produced at the cathode resulting from carbon transfer, it is preferred that the electrolytic cell includes a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms 25 positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

The membrane may be formed from any suitable material.

30 Preferably the membrane is formed from a solid electrolyte.

One solid electrolyte tested by the applicant is 35 yttria stabilised zirconia.

According to the present invention there is also

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provided an electrolytic cell as described above and operating in accordance with the above described method.

5 The present invention is described further with reference to the following example.

### I. Experimental Method and Electrolytic Cell

The electrolytic cell is shown in Figure 1.

10

With reference to Figure 1, the electrochemical cell included a graphite crucible equipped with a graphite lid. The crucible was used as the cell anode. A stainless steel rod was used to secure electrical contact between a d/c power supply and the crucible. The cell cathode consisted of Kanthal or platinum wire connected at one end to the power supply and TiO<sub>2</sub> pellets suspended from the other end of the wire. An alumina tube was used as an insulator around the cathode. The cell electrolyte was a commercially available source of CaCl<sub>2</sub>, namely calcium chloride dihydrate, that partially decomposed on heating at the operating temperature of the cell and produced CaO. A thermocouple was immersed in the electrolyte in close proximity to the pellets.

25

Two types of pellets were used. One type was slip-cast and the other type was pressed. Both types of pellets were made from analytical grade TiO<sub>2</sub> powder. Both types of pellets were sintered in air at 850°C. One pressed and one slip-cast pellet were used in the experiment.

30  
35 The cell was positioned in a furnace and the experiment was conducted at 950°C. Voltages up to 3V were applied between the crucible wall and the Kanthal or platinum wire. The voltage of 3V is below the potential at which Cl<sup>-</sup> anions can deposit on the anode at that

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temperature. In addition, the voltage of 3V is above the decomposition potential of CaO and below the decomposition potential of CaCl<sub>2</sub>.

5       The power-supply maintained a constant voltage throughout the experiment. The voltage and resulting cell current were logged using LabVIEW (TM) data acquisition software.

10       At the end of the experiment the cell was removed from the furnace and quenched in water. The solid CaCl<sub>2</sub> was dissolved by water and the two pellets were recovered.

15       II.       Experimental Results

20       With reference to Figures 2 and 3, the constant voltage (3V) used in the experiment produced an initial current of approximately 1.2A. A continuous drop in the current was observed during the initial 2 hours. After that a gradual increase in the current up to 1A was observed.

25       SEM images of the cross-sections of the two recovered pellets are shown in Figures 4 and 5. The SEM images indicate the presence of metallic titanium in both pellets, thereby establishing that the method successfully electrochemically reduced titania.

30       The presence of virtually pure metallic titanium in both pellets was confirmed by EPMA analysis. The analysis also showed areas of partially reduced titania. The EPMA results are shown in Figures 6 and 7.

35       Carbon was detected at various locations within the pellets and its content varied up to 18wt%.

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Many modifications may be made to the present invention as described above without departing from the spirit and scope of the invention.

5 By way of example, whilst the above description of the invention focuses on reduction of titania, the invention is not so limited and extends to reduction of other titanium oxides and to oxides of other metals and alloys. Examples of other potentially important metals  
10 are aluminium, silicon, germanium, zirconium, hafnium, magnesium and molybdenum.

Furthermore, whilst the above description focuses on  $\text{CaCl}_2$ -based electrolyte, the invention is not so limited  
15 and extends to any other suitable electrolytes (and mixtures of electrolytes). Generally, suitable electrolytes will be salts and oxides that are soluble in salts. One example of a potentially suitable electrolyte is  $\text{BaCl}_2$ .

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CLAIMS:

1. A method of reducing a metal oxide in a solid state in an electrolytic cell, which electrolytic cell includes an anode, a cathode, a molten electrolyte, the electrolyte includes cations of a metal that is capable of chemically reducing the metal oxide, and the metal oxide in a solid state is immersed in the electrolyte, and which method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide can deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

15

2. The method defined in claim 1 includes operating the cell that is above the potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode so that the metal deposits on the cathode.

20

3. The method defined in claim 2 wherein the metal deposited on the cathode is soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the metal oxide.

25

4. The method defined in any one of the preceding claims wherein the metal oxide is a titanium oxide, the electrolyte is a CaCl<sub>2</sub>-based electrolyte that includes CaO as one of the constituents of the electrolyte, and the cell potential is above a potential at which Ca metal can deposit on the cathode.

30

5. The method defined in claim 4 wherein the cell potential is below the decomposition potential for CaCl<sub>2</sub> to minimise forming Cl<sub>2</sub> gas at the anode.

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6. The method defined in claim 4 or claim 5 wherein the cell potential is less than or equal to 3.5V in a cell operating with the electrolyte at 600-1100°C.

5 7. The method defined in any one of claims 4 to 6 wherein the cell potential is at least 1.3V in a cell operating with the electrolyte at 600-1100°C.

10 8. The method defined in any one of claims 4 to 7 wherein the CaCl<sub>2</sub>-based electrolyte is a commercially available source of CaCl<sub>2</sub> that forms CaO on heating or otherwise includes CaO.

15 9. The method defined in any one of claims 4 to 7 wherein the CaCl<sub>2</sub>-based electrolyte includes CaCl<sub>2</sub> and CaO that are added separately or pre-mixed to form the electrolyte.

20 10. The method defined in any one of the preceding claims wherein the anode is graphite.

25 11. The method defined in any one of the preceding claims wherein the anode is graphite and the electrolytic cell includes a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

30 12. The method defined in any one of the preceding claims wherein the cathode is formed at least in part from the metal oxide.

35 13. An electrolytic cell reducing a metal oxide in a solid state, which electrolytic cell includes an anode, a cathode, a molten electrolyte, which electrolyte includes cations of a metal that is capable of chemically

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reducing the metal oxide, and a metal oxide in a solid state immersed in the electrolyte, and which electrolytic cell operates at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

14. The cell defined in claim 12 wherein the cathode is formed at least in part from the metal oxide.

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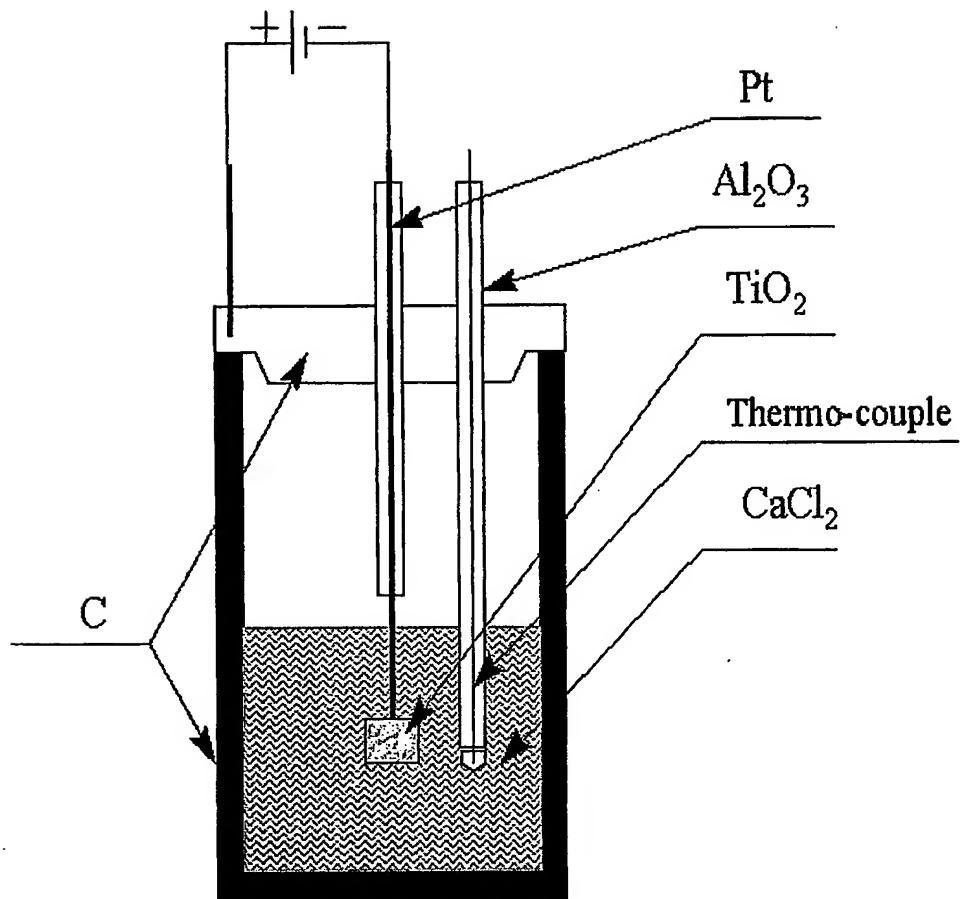


Fig. 1 Schematic of the experimental set up

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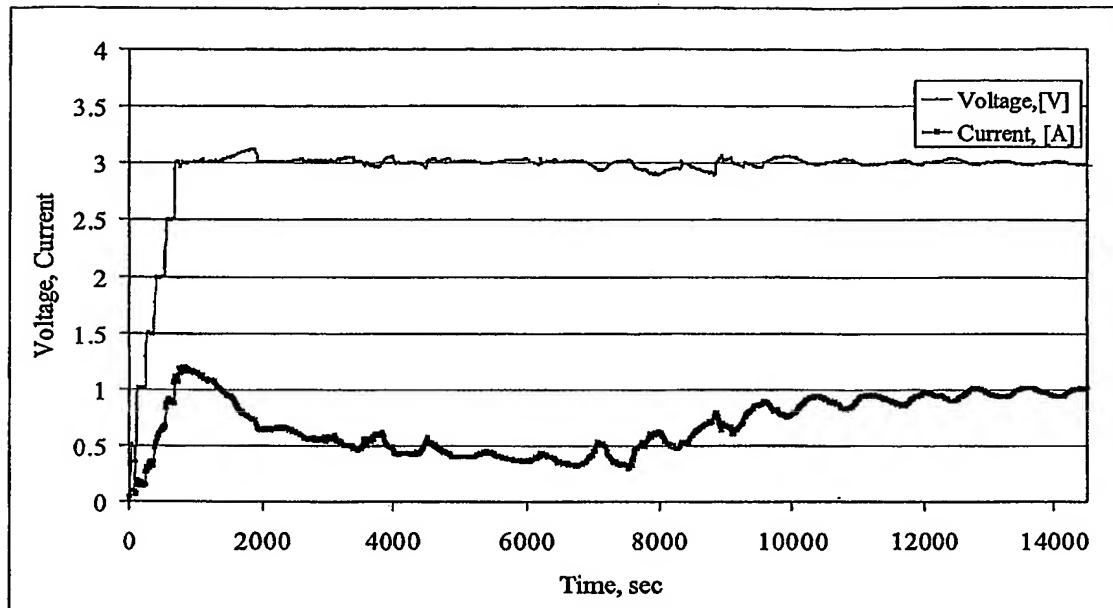


Fig 2. Variation of the applied potential and current during the run

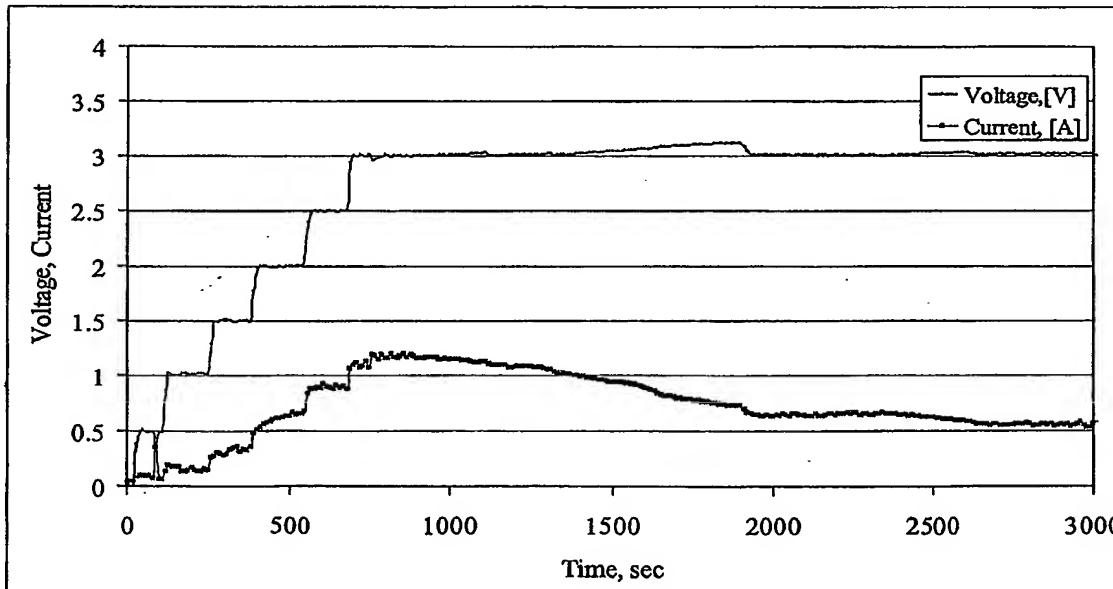
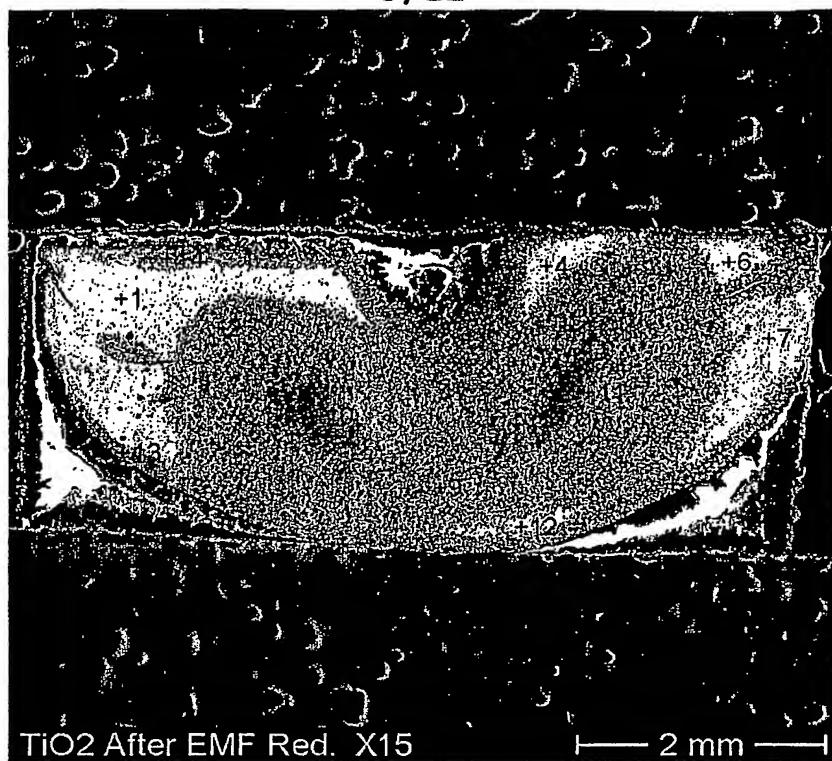
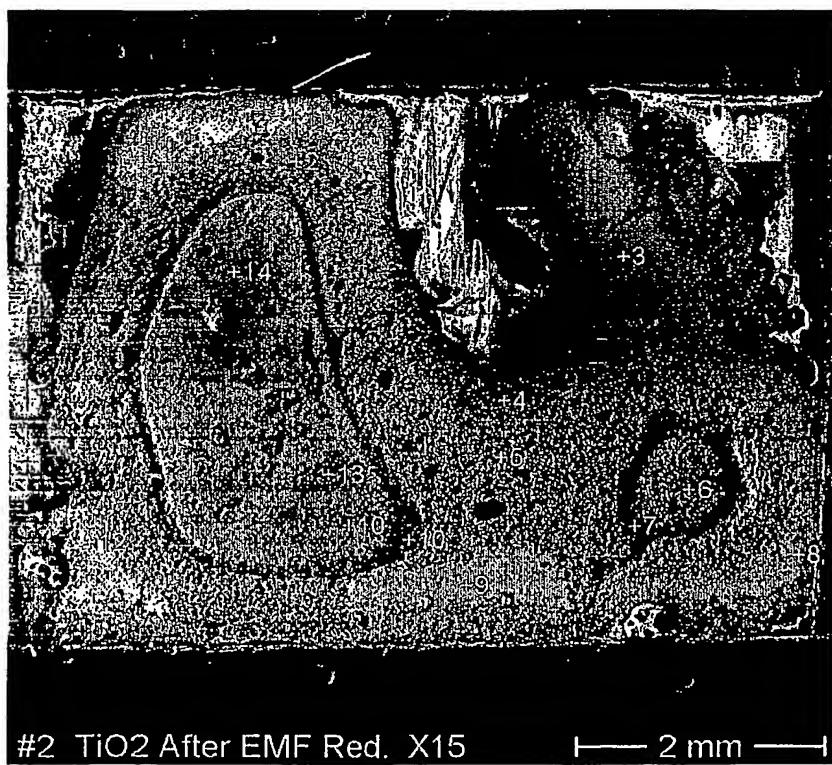


Fig 3. Variation of the applied potential and current in the initial stage of the run

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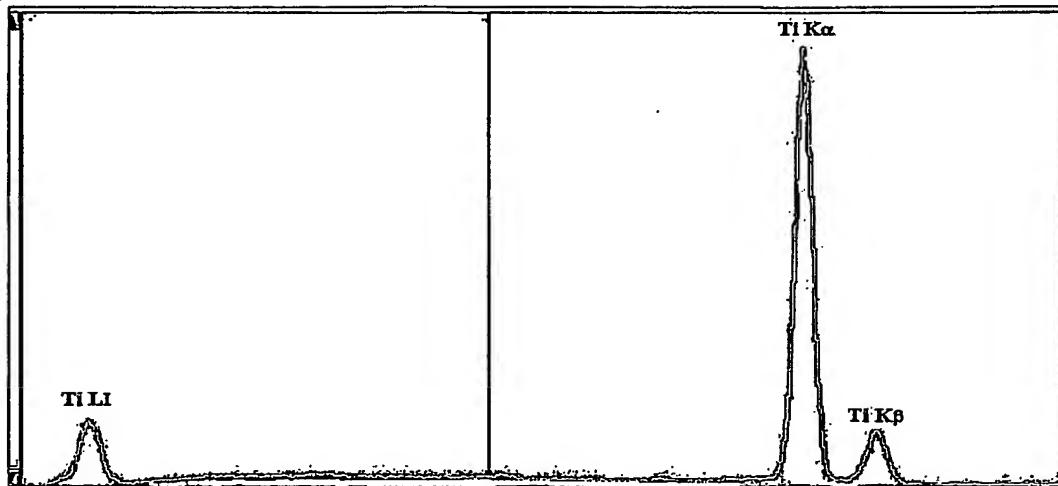


**Fig 4. SEM image of the horizontal cross-section of Pellet 1 after the run**

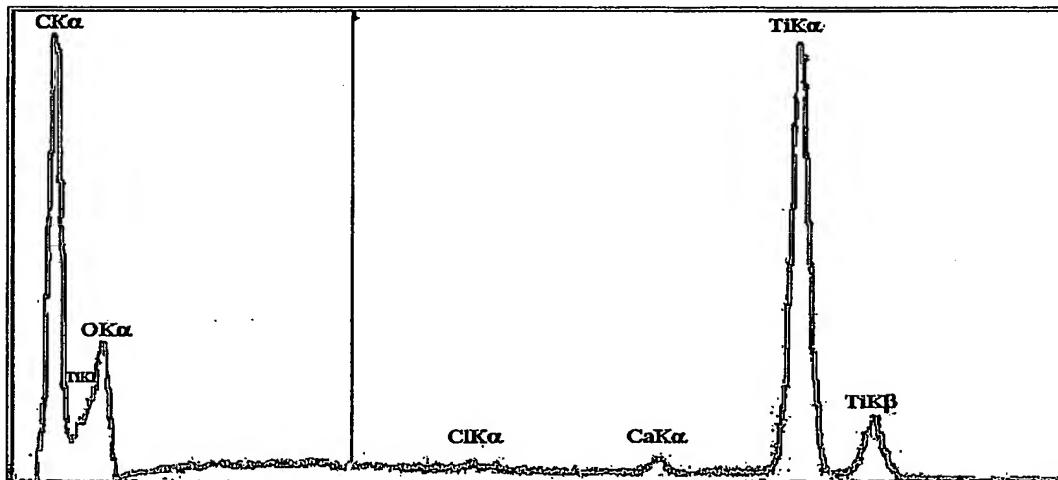


**Fig. 5. SEM image of a horizontal cross-section of Pellet 2 after the run**

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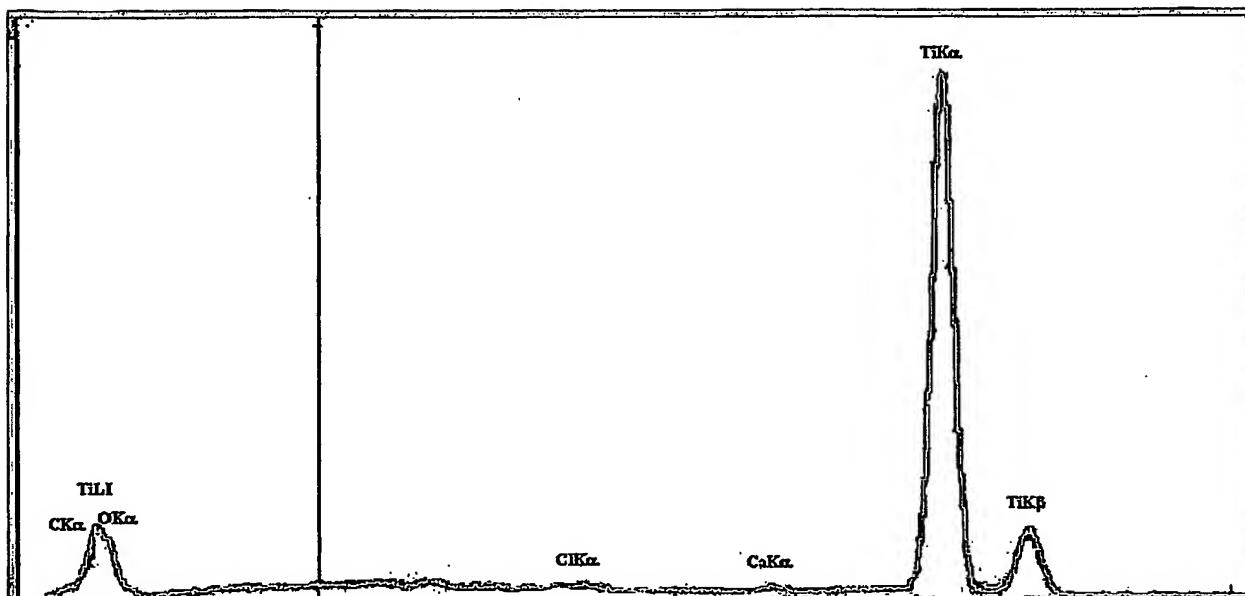
Point 1



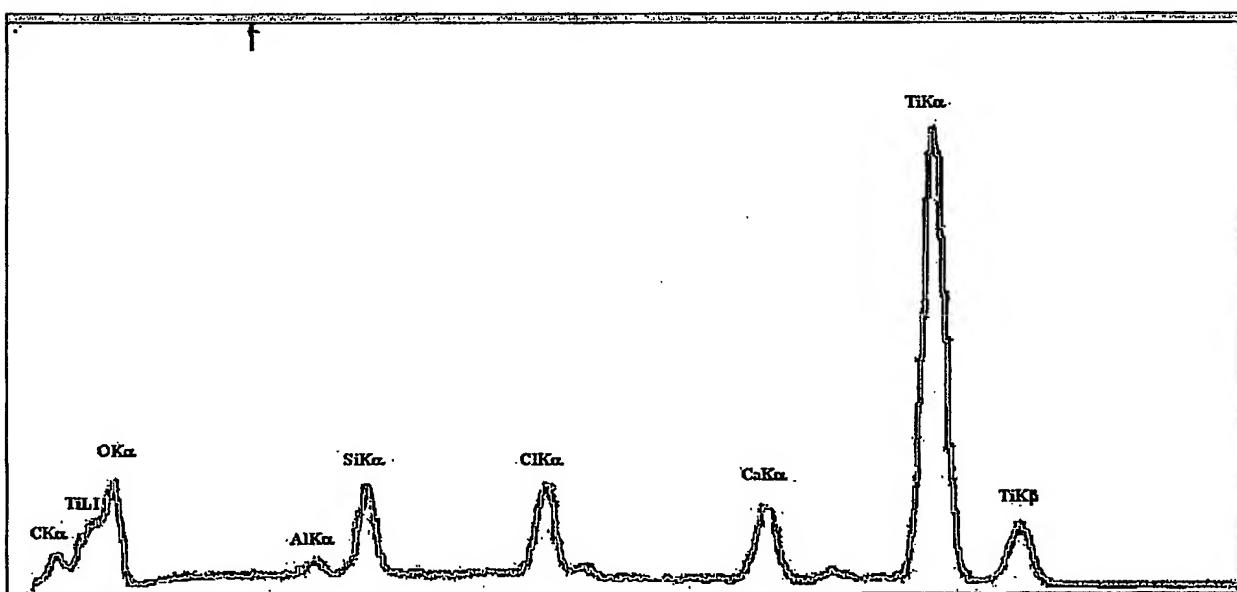
Point 2

Fig. 6. EPMA analysis of Pellet 1 (Pressed)

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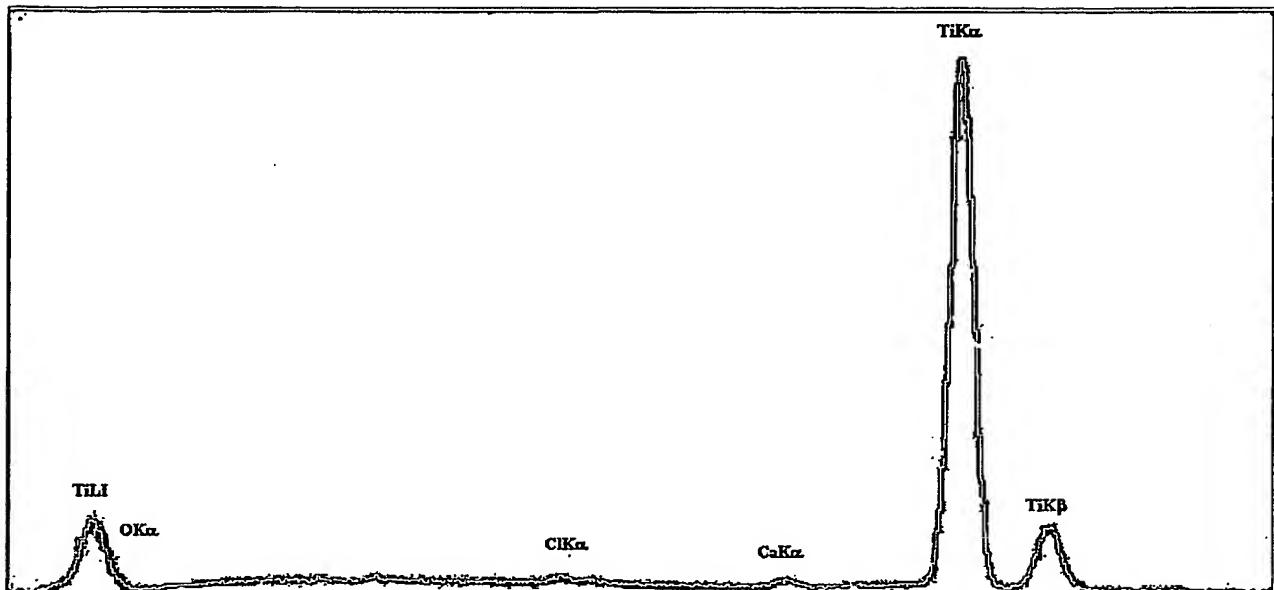
Point 1



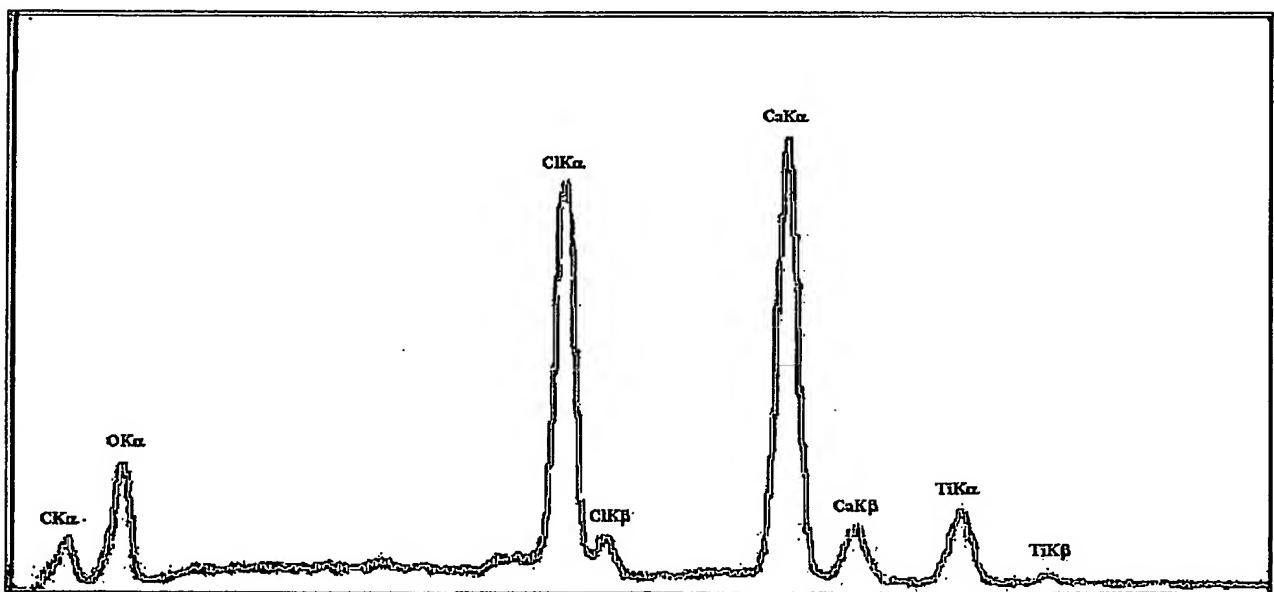
Point 2

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) - Part 1

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Point 3



Point 4

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) - Part 2

7/11

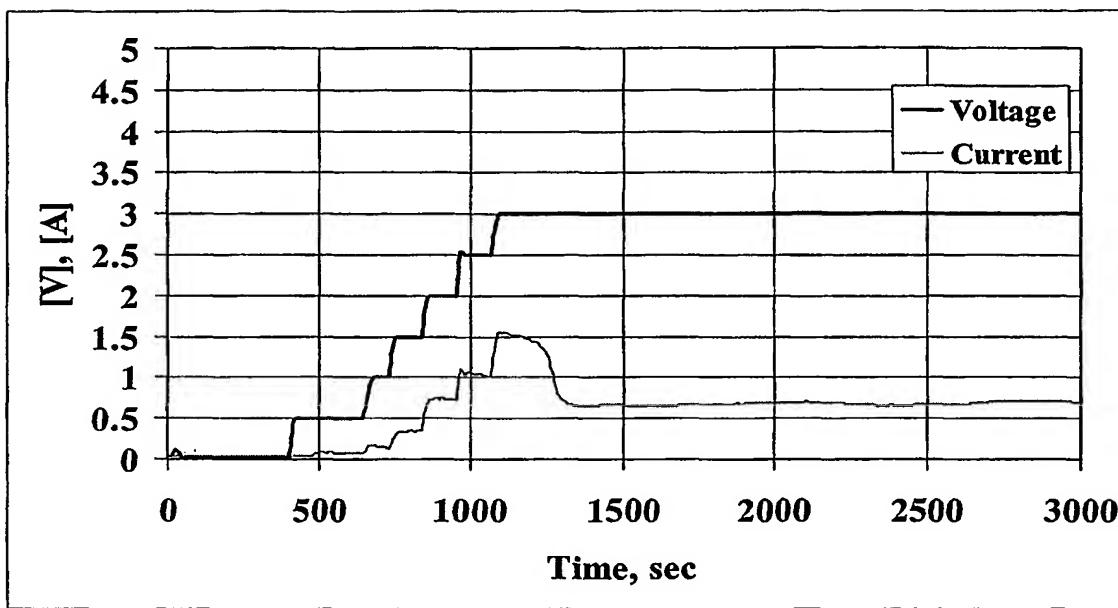


Fig. 8. Variation of the applied potential and current in the initial stage of the run

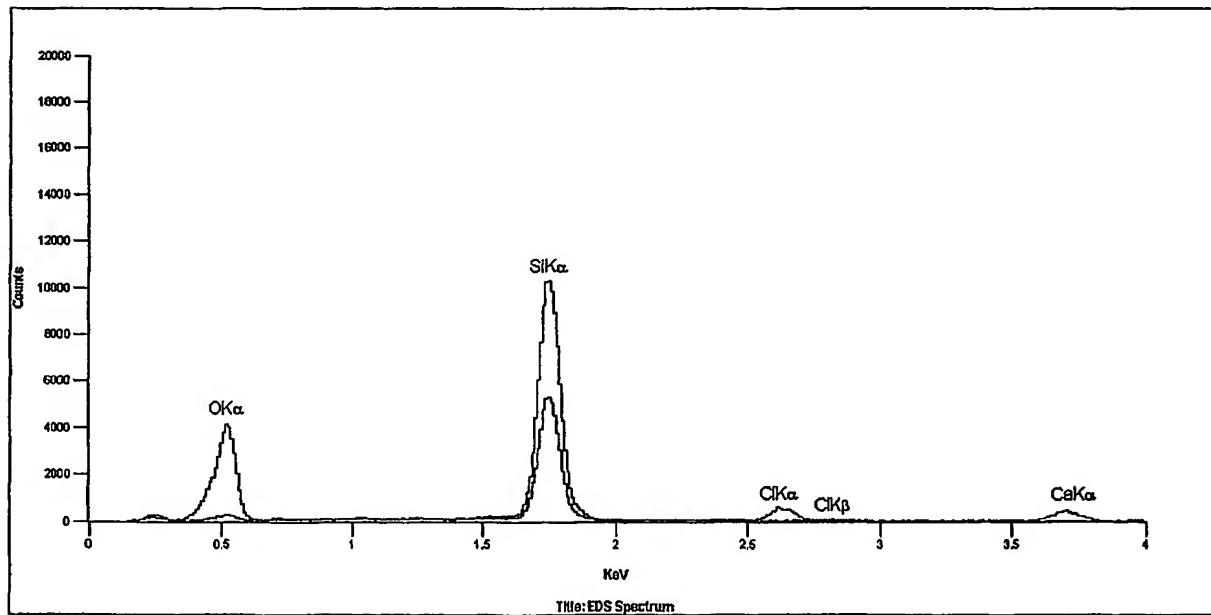
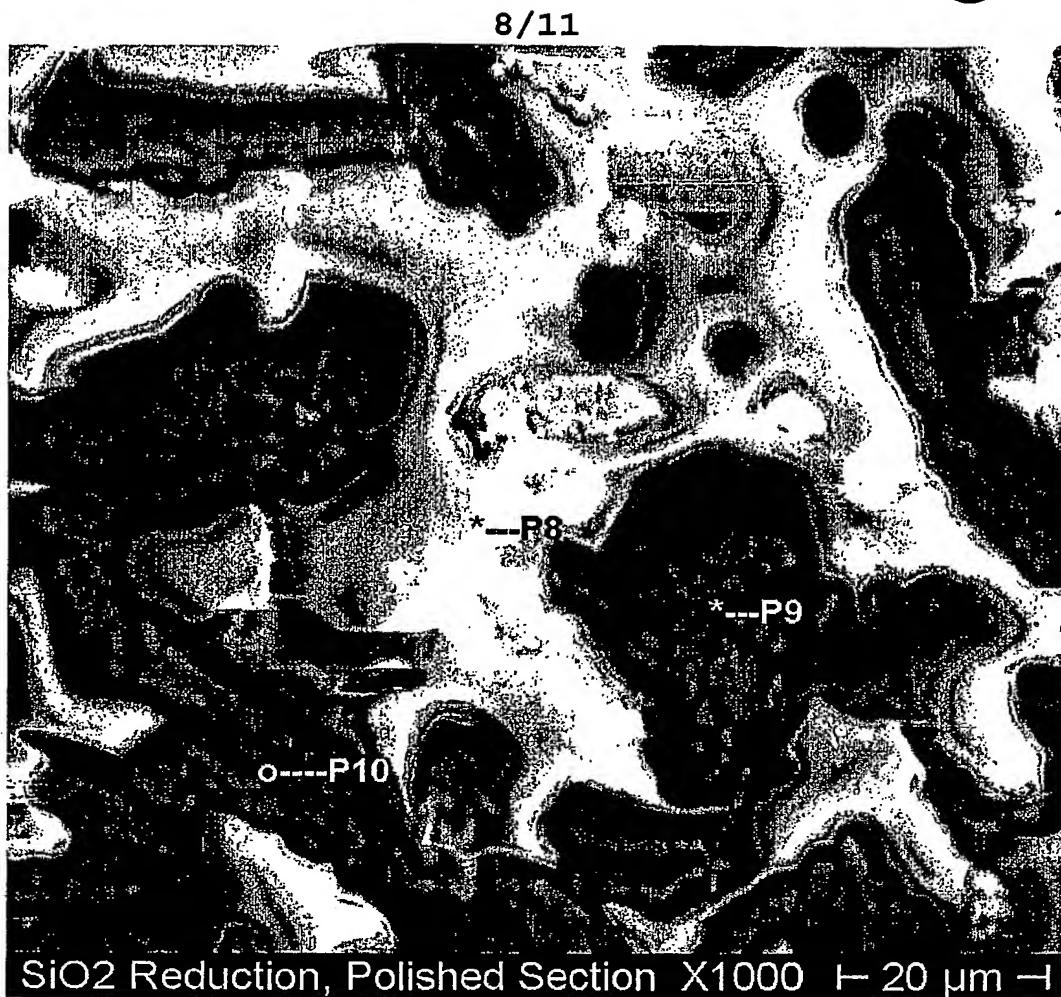


Fig. 9. Comparison of the spectrum of pure  $\text{SiO}_2$  with the one of the surface of the sample after reduction



$\text{SiO}_2$  Reduction, Polished Section  $\times 1000 \quad 20 \mu\text{m}$

Fig. 10. Appearance of the structure of the  $\text{SiO}_2$  pellet after reduction

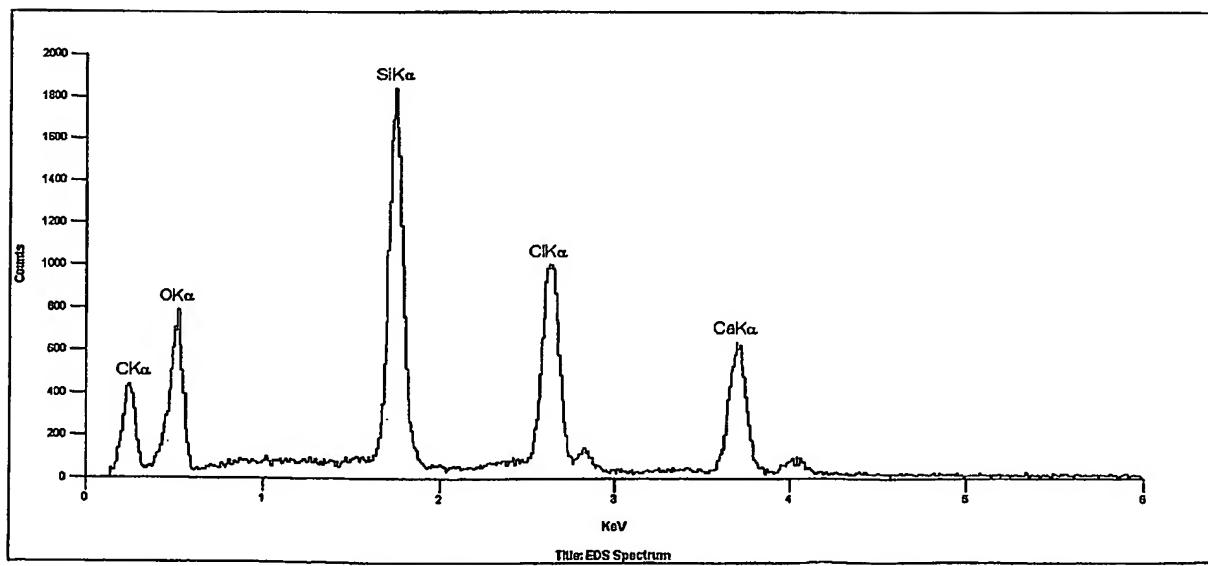


Fig. 11. Spectrum at point 8 in Figure 10.

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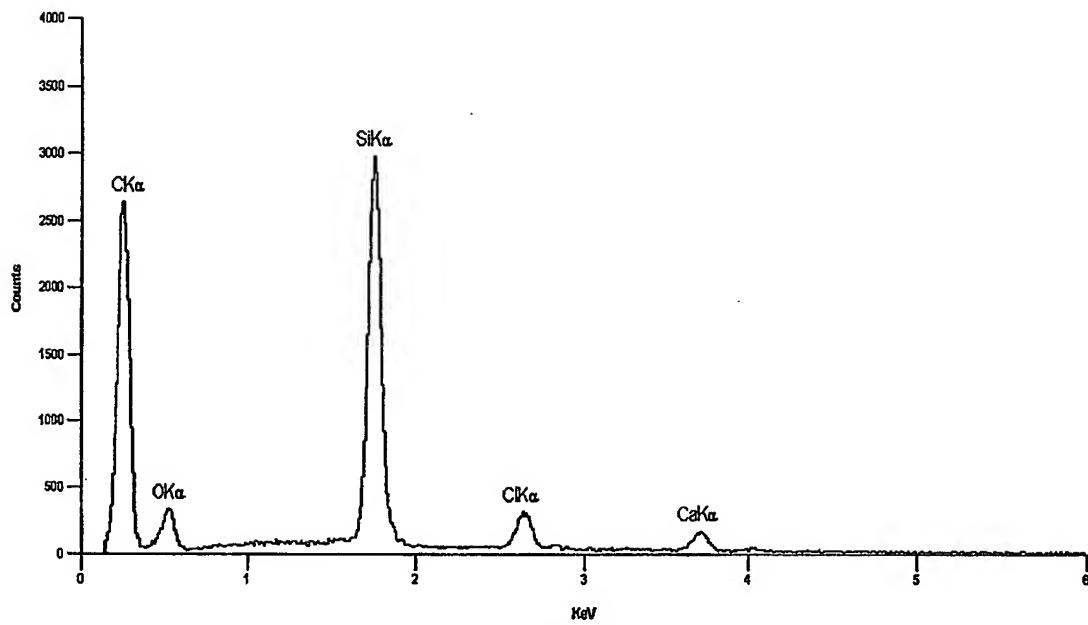


Fig. 12. Spectrum at point 10 in Figure 10.

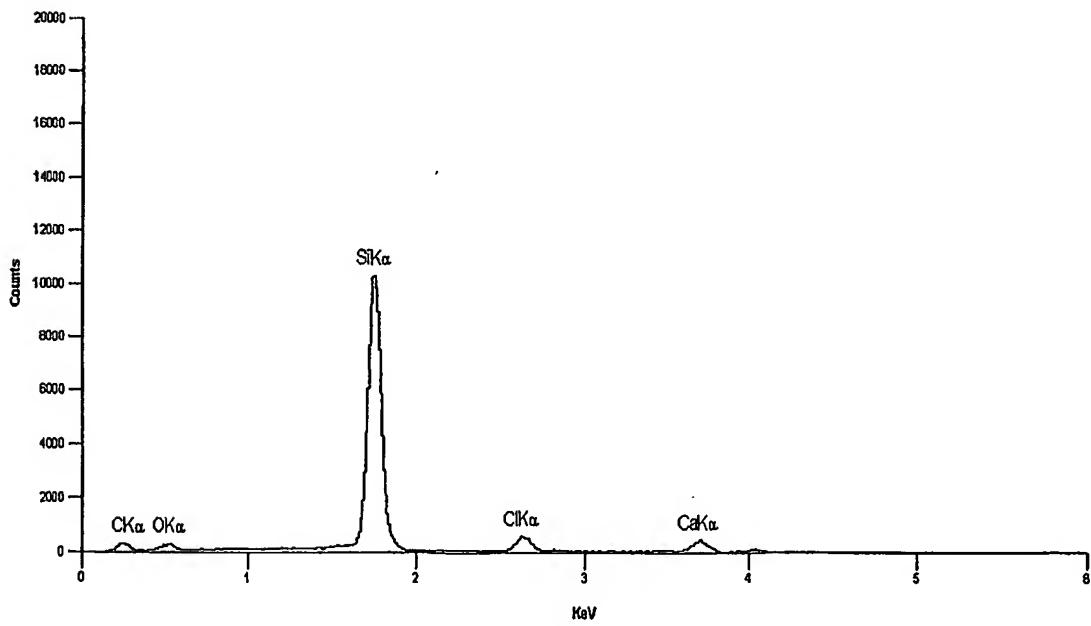


Fig. 13. Spectrum at point 10 in Figure 10.

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Si Crystal X4000

— 6  $\mu\text{m}$  —

Fig. 14. Silicon crystal found in the pellet after reduction

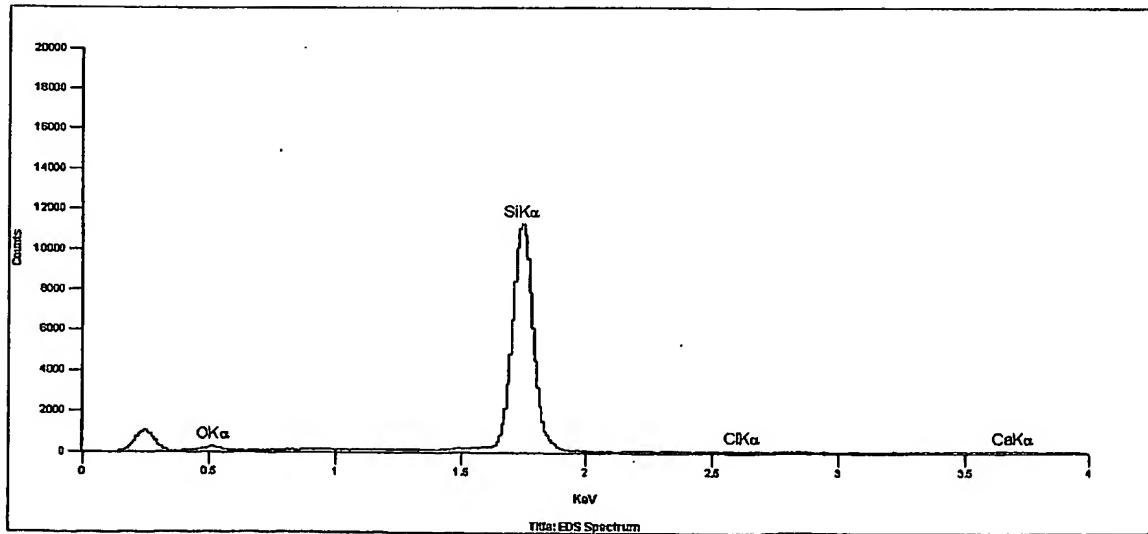


Fig. 15. Spectrum of the crystal in Figure 14.

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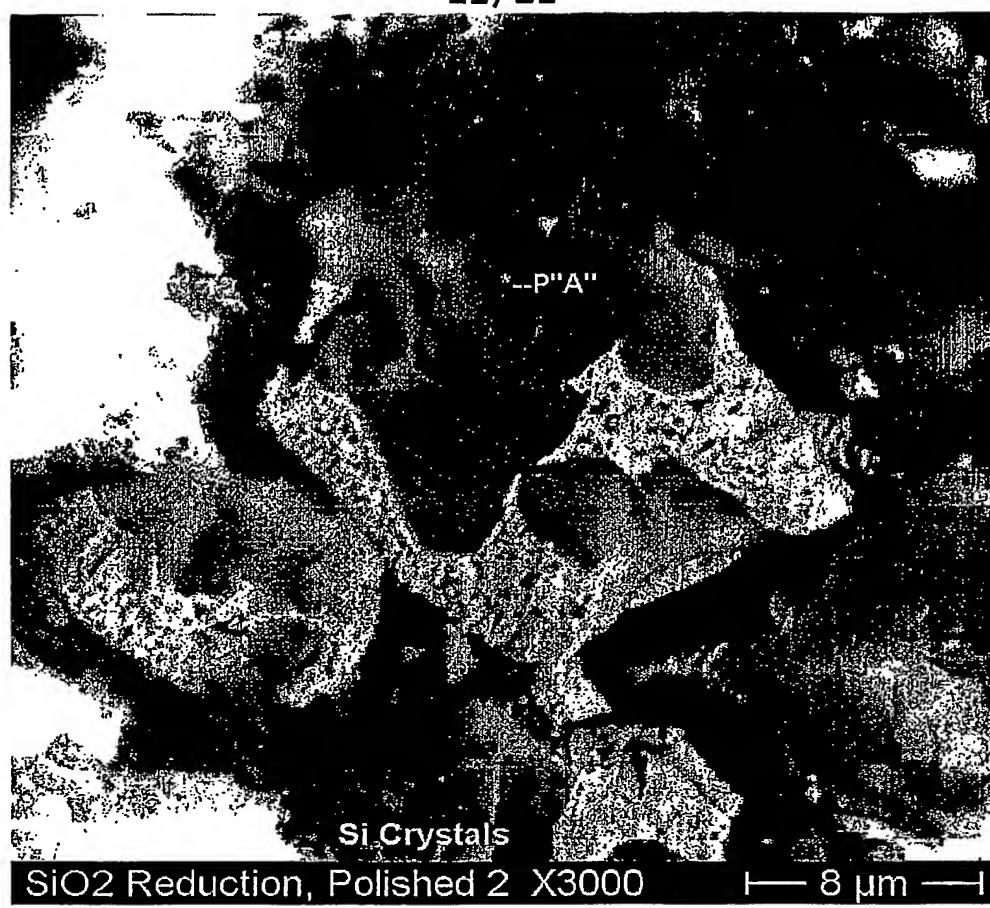


Fig. 16. Silicon crystal found in the pellet after reduction

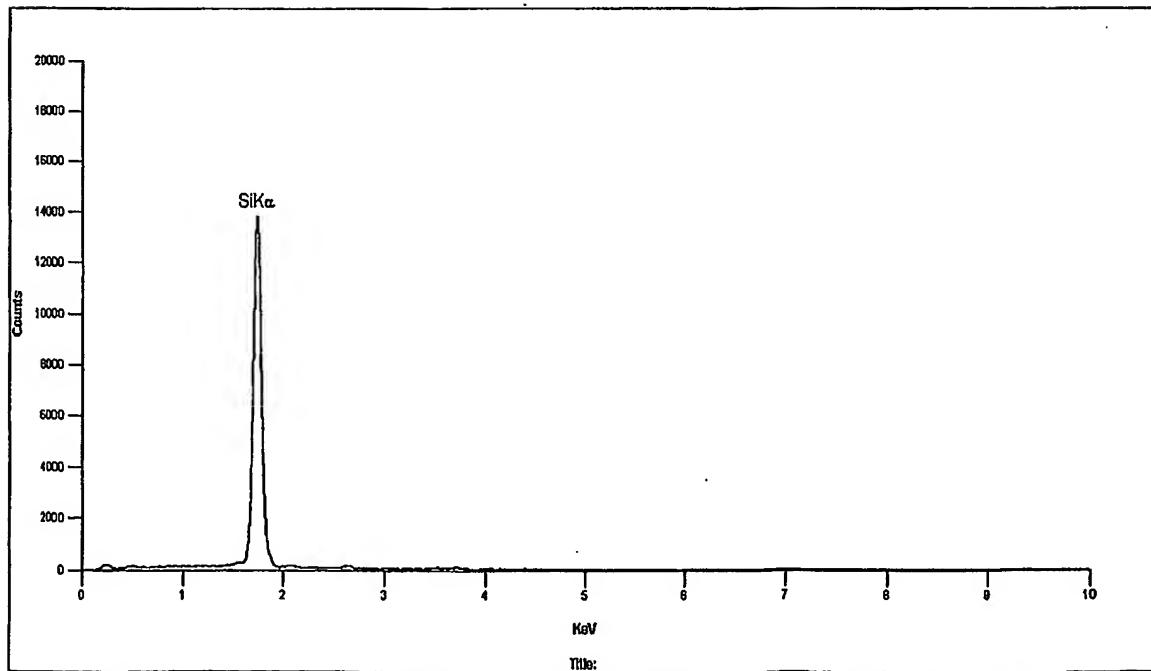


Fig. 17. Spectrum at point A in Figure 16.

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00306

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. <sup>7</sup>: C25C 3/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

DWPI: C25C 5/04, C22B 34/12, and KEYWORDS: reduc+, electro+

E-space: C25C 3/00

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 03/002785 A (BHP BILLITON INNOVATION PTY LTD) 9 January 2003 Whole document, especially claims 1-9	1-14
P,X	WO 03/016594 A (BHP BILLITON INNOVATION PTY LTD) 27 February 2003 Pages 5, 9-12, and claims	1-14
P,X	WO 02/083993 A (BHP BILLITON INNOVATION PTY LTD) 24 October 2002 Whole document	1-14

 Further documents are listed in the continuation of Box C See patent family annex

* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search  
16 April 2003

Date of mailing of the international search report

30 APR 2003

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PO BOX 200, WODEN ACT 2600, AUSTRALIA  
E-mail address: pct@ipaaustralia.gov.au  
Facsimile No. (02) 6285 3929

Authorized officer

THARU FERNANDO

Telephone No : (02) 6283 2486

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00306

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2359564 A (THE SECRETARY OF STATE FOR DEFENCE) 29 August 2001 Whole document	1-14
A	WO 99/64638 A (CAMBRIDGE UNIVERSITY TECHNICAL SERVICES LIMITED) 16 December 1999 Whole document	1-14
A	US 6074545 A (GINATTA) 13 June 2000 Whole document	1-14

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU03/00306

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member			
WO	03002785	NONE				
WO	03016594	NONE				
WO	02083993	NONE				
WO	9964638	AU 42770/99 CZ 20004476 NO 20006154	BR 9910939 EP 1088113 PL 344678		CA 2334237 HU 200102934	
GB	2359564	AU 200133871 EP 1257677 GB 2376241 WO 200162995	AU 200133876 EP 1257678 US 2003057101 WO 200162996		AU 200133890 EP 1257679 WO 200162994 GB 2362164	
US	6074545	AU 81918/98 IT TO NZ 337553	BR 9807156 970080 WO 9833956		EP 958409 NO 993455 ZA 9800897	
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